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The Behavior of Microdisks and Microring Electrodes. Prediction of the Amperometric Response of Microdisks and of the steady state for c.e. and e.c. catalytic reactions by application of Neumann's Integral Theorem

by

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Abstract

It is shown that the chronoamperometric response at microdisk electrodes can be derived from Neumann's integral theorem of two parameters. The form of the transients can be predicted for a wide range of boundary conditions and this is illustrated by the relaxation behavior of irreversible reactions in addition to that of the widely investigated example of zero surface concentration of the reactant. Corrections to the transients due to the tertiary current distribution are derived for relaxation experiments and it is shown that the methods developed can also be applied to linear sweep voltammetry.

The steady state behavior of c.e. and e.c. catalytic reactions is formally similar to the chronoamperometry of irreversible electrode reactions and it is shown that complete descriptions can be obtained for the voltammetry of such systems. Keywords: [illegible]

THE BEHAVIOR OF MICRODISK AND MICRORING ELECTRODES. PREDICTION OF THE CHRONOAMPEROMETRIC RESPONSE OF MICRODISKS AND OF THE STEADY STATE FOR c.e. AND e.c. CATALYTIC REACTIONS BY APPLICATION OF NEUMANN'S INTEGRAL THEOREM.

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Introduction

We have shown recently that the steady-state behavior of simple reactions at microdisk electrodes can be predicted[1,2] by the application of Neumann's integral theorem[3]. The concentration distribution for a reactant (or product) in such a reaction is governed by

$$D \frac{\partial^2 C}{\partial r^2} + \frac{D}{r} \frac{\partial C}{\partial r} + D \frac{\partial^2 C}{\partial z^2} = 0 \qquad [1]$$

and we obtain

$$C(r,z) = \int_0^\infty \alpha d\alpha \int_0^a \frac{\exp(-\alpha z)}{\alpha} \frac{Q(\rho)}{D} J_0(\alpha r) J_0(\alpha\rho)\rho d\rho \qquad [2]$$

Equation [2] makes a formal linkage between the distribution of sources, $Q(\rho)$, (or sinks) at the radial position ρ and the concentration throughout space. We have shown that the use of the simple form for the distribution of sinks

$$-Q(\theta) = \frac{-1}{a\cos(\theta)} \left\{ c_0 + c_1 \cos(\theta) + c_2 \cos(2\theta) + \cdots + c_n \cos(n\theta) \right\} \qquad [3]$$

where

$$\rho = a \sin(\theta) \qquad [4]$$

leads to the recovery of known results[4,5] (derived by the application of the discontinuous integrals of Bessel functions) for constant surface concentrations provided we assume

$$c_1 = c_2 = c_3 = \cdots = c_n = 0 \qquad [5]$$

and

$$c_0 = \frac{2D}{\pi}\left(C^{\infty} - C^{s}\right) \qquad [6]$$

and of constant, uniform, surface flux provided we assume

$$c_0 = c_2 = c_3 = \cdots = c_n = 0 \qquad [7]$$

and

$$c_1 = Qa \qquad [8]$$

It has also been shown that the reexpression of [3] in the form

$$-Q(\theta) = \frac{-1}{a\cos(\theta)}\left(d_0 + d_1\cos(\theta) + \cdots + d_n\cos^n(\theta)\right) \qquad [9]$$

is particularly useful in discussing the application of more general boundary conditions such as

$$D\left(\frac{\partial C}{\partial z}\right) = kC^s, \; 0 < r < a, \; z = 0 \qquad [10]$$

The use of [9] in [2] leads to the simple result

$$C(r) = -\frac{\pi^{1/2}}{2D}\sum_{j=0}^{n} d_j \frac{\Gamma\left(\frac{j+1}{2}\right)}{\Gamma\left(\frac{j+2}{2}\right)} {}_2F_1\left\{\frac{1}{2}, -\frac{j}{2}; 1; \frac{r^2}{a^2}\right\} \qquad [11]$$

(at $z = 0$) where Γ is the gamma function and ${}_2F_1$ denotes the appropriate hypergeometric function. Application of [11] at (n+1) radial positions in any particular boundary condition (such as [10]) then allows the evaluation of the unknown coefficients in [9] thereby giving a complete solution for any particular problem. The results obtained by the application of Neumann's integral theorem has been related also to results derived by an extension[6] of the application of the discontinuous integrals of Bessel functions[4,5]. We have shown also that the use of Neumann's integral allows the evaluation of the effects of the distribution of potential in the solution (the tertiary current distribution) and of the non-linearities in the concentration terms of the electrode reactions[1,2].

In this paper we extend the approach to the discussion of the chronoamperometric response of microdisk electrodes, comment on the effects of the distribution of potential in the solution, and outline the analysis of linear sweep voltammetric experiments. In view of the formal similarity of the derived equations to those obtained for the steady state behavior of reactions following the c.e. and e.c. mechanisms, we also derive the relevant results for these reaction pathways.

Chronoamperometry

We consider first of all the behavior of a simple diffusion controlled reaction where mass transfer of the reactant is controlled by

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial r^2} + \frac{D}{r}\frac{\partial C}{\partial r} + D\frac{\partial^2 C}{\partial z^2} \qquad [12]$$

subject to the initial condition

$$C = C^{\infty},\ 0 < r < \infty,\ z > 0,\ t = 0 \qquad [13]$$

and the boundary conditions

$$C = 0,\ 0 < r < a,\ z = 0,\ t > 0 \qquad [14]$$

$$D\frac{\partial C}{\partial z} = 0,\ r > a,\ z = 0,\ t > 0 \qquad [15]$$

Laplace transformation of [12] subject to [13] gives

$$\frac{\partial^2 \bar{C}}{\partial r^2} + \frac{1}{r}\frac{\partial \bar{C}}{\partial r} + \frac{\partial^2 \bar{C}}{\partial z^2} - \frac{s}{D}\bar{C} + \frac{C^{\infty}}{D} = 0 \qquad [16]$$

where s is the variable of the Laplace transformation. The solution of [16] can therefore be expressed in terms of Neumann's integral of two parameters

(ρ, s) using $Q(\rho, s)$ as

$$\bar{C}(r,z,s) = \frac{C^{\infty}}{s} + \int_0^{\infty} \alpha d\alpha \int_0^{a} \frac{\exp\left(-\left[\alpha^2 + \frac{s}{D}\right]^{1/2} z\right)}{\left[\alpha^2 + \frac{s}{D}\right]^{1/2}} \frac{Q(\rho,s)}{D} J_0(\alpha r) J_0(\alpha\rho)\rho d\rho \qquad [17]$$

By analogy with the expansion [9] used to describe the distribution of sinks in the steady state, we write

$$-\bar{Q}(\theta) = \frac{-1}{a\cos(\theta)} \left(\bar{d}_0(s) + \bar{d}_1(s)\cos(\theta) + \cdots + \bar{d}_n(s)\cos^n(\theta) \right) \qquad [18]$$

where all the coefficients d_j are now functions of s. Substitution of [18] and [4] in [17] gives at $z = 0$

$$\bar{C}(r,s) = \frac{C^{\infty}}{s} - \frac{a}{D} \int_0^{\infty} \frac{J_0(\alpha r)\alpha d\alpha}{\left[\alpha^2 + \frac{s}{D}\right]^{1/2}} \int_0^{\pi/2} \sum_{j=0}^{n} d_j(s) J_0(\alpha a \sin(\theta))\sin(\theta)\cos^j(\theta) d\theta$$

$$= \frac{C^\infty}{s} - \frac{1}{Da}\sum_{j=0}^{n} \bar{d}_j(s)e_j \int_0^\infty \frac{J_0(\alpha r)\, J_{\left(\frac{j+1}{2}\right)}(\alpha a)\, d(\alpha a)}{\left[\alpha^2 + \frac{s}{D}\right]^{1/2} (\alpha a)^{((j-1)/2)}} \qquad [19]$$

for a distribution of sinks $\bar{Q}(\theta)$ over the surface where

$$e_j = 2^{((j-1)/2)}\Gamma((j+1)/2) \qquad [20]$$

The coefficients $d_j(s)$ can then be obtained by substituting [18] and [19] into the Laplace transform of the boundary condition appropriate to the particular form of the experiment. For example, for the simple condition

$$\bar{C} = 0,\ 0 < r < a,\ z = 0 \qquad [21]$$

(cf [14]) we solve the set of equations

$$\sum_{j=0}^{n} \frac{\bar{d}_j(s)e_j}{Da} \int_0^\infty \frac{J_0(\alpha r_k)\, J_{\left(\frac{j+1}{2}\right)}(\alpha a)\, d(\alpha a)}{\left[\alpha^2 + \frac{s}{D}\right]^{1/2} (\alpha a)^{((j-1)/2)}} = \frac{1}{s} \qquad [22]$$

at (n+1) radial positions. We therefore obtain the unknown coefficients as functions of the parameter s. Substitution of these coefficients into [18] and integration over the radius of the disk then gives the Laplace transform of the total rate of reaction, $\bar{R}$,

$$\bar{R} = 2\pi D \int_0^a \left(\frac{\partial \bar{C}}{\partial z}\right)_{z=0} r\,dr = 2\pi \sum_{j=0}^{n} \int_0^a \bar{d}_j(s) \left(\frac{a^2-r^2}{a^2}\right)^{j/2} \frac{r\,dr}{\left(a^2-r^2\right)^{1/2}}$$

$$= 2\pi a \sum_{j=0}^{n} \int_0^{\pi/2} \bar{d}_j(s) \cos^j(\theta) \sin(\theta)\, d\theta$$

$$= 2\pi a \sum_{j=0}^{n} \frac{\bar{d}_j(s)}{(j+1)} \qquad [23]$$

Numerical inversion of [23] gives the total rate of reaction in the t-domain.

An alternative procedure is to invert [22] to the relevant convolution integrals

$$\sum_{j=0}^{n} \frac{e_j}{D^{1/2}\pi^{1/2}a} \int_0^t \int_0^\infty d_j(t-\tau)\ \frac{\exp(-D\alpha^2\tau)}{\tau^{1/2}}\ \frac{J_0(\alpha r_k)\ J_{\left(\frac{j+1}{2}\right)}(\alpha a)\ d(\alpha a)\,d\tau}{(\alpha a)^{((j-1)/2)}}$$

$$= \sum_{j=0}^{n} \frac{e_j}{D^{1/2}\pi^{1/2}a} \int_0^t \int_0^\infty d_j(\tau)\, \frac{\exp(-D\alpha^2(t-\tau))}{(t-\tau)^{1/2}}\, \frac{J_0(\alpha r_k)\, J_{\left(\frac{j+1}{2}\right)}(\alpha a)\, d(\alpha a)\, d\tau}{(\alpha a)^{((j-1)/2)}}$$

$$= 1 \qquad [24]$$

In the numerical integration over say l intervals of $\Delta\tau$ we then have to solve the set of Equations [24] for the values of d_j in the lth interval. This forward integration is simplified by the fact that we know that the system follows the Cottrell equation at short times(7) for which at sufficiently large s

$$d_1(s) = \frac{aC^\infty}{s^{1/2}} \qquad [25]$$

and

$$d_0 = d_2 = d_3 = \cdot \cdot \cdot \cdot = d_n = 0 \qquad [26]$$

Other boundary conditions; the tertiary current distribution; linear sweep voltammetry.

We have pointed out elsewhere that the application of the boundary condition [14] (or, more generally, of a constant surface concentration boundary condition) is unrealistic as the flux would have to become infinite at the edges of the disk(1,2,4,8); see also(6). However, the flux cannot become infinite for two reasons: firstly because the rate constant governin

the electrochemical reaction must itself be finite and, secondly, because an infinite rate of reaction would also require an infinite overpotential at he edges of the disk. The current distribution must therefore be more uniform than that predicted using the boundary condition [14] under most experimental conditions (the tertiary current distribution).

As the application of Neumann's integral theorem provides a link between the assumed form of the flux distribution, Equation [18], and the concentration distribution, Equation [19], it is straightforward to assess the effects of the boundary conditions more complex than [14]. We restict attention here to irreversible reactions which are described by [10]. Substitution of [19] into the Laplace transform of [10] gives

$$D\left(\frac{\partial\bar{C}(r,s)}{\partial s}\right) =$$

$$\frac{1}{\left(a^2-r^2\right)^{1/2}}\left[\bar{d}_0(s) + \bar{d}_1(s)\left(\frac{a^2-r^2}{a^2}\right)^{1/2} + \bar{d}_2(s)\left(\frac{a^2-r^2}{a^2}\right) + \cdots + \bar{d}_n(s)\left(\frac{a^2-r^2}{a^2}\right)^{n/2}\right]$$

$$= \frac{1}{a\cos(\theta)}\left(\bar{d}_0(s) + \bar{d}_1(s)\cos(\theta) + \cdots + \bar{d}_n(s)\cos^n(\theta)\right)$$

$$= \frac{kC^{\infty}}{s} - \frac{k}{Da}\sum_{j=0}^{n} \bar{d}_j(s)e_j \int_0^{\infty} \frac{J_0(\alpha r)\, J_{\left(\frac{j+1}{2}\right)}(\alpha a)\, d(\alpha a)}{\left[\alpha^2 + \frac{s}{D}\right]^{1/2} (\alpha a)^{((j-1)/2)}} \qquad [27]$$

The dependence of the coefficients d_j on s can therefore be obtained as for the case of zero surface concentration governed by Equation [22]. The distribution of the flux and concentration and the total rate of reaction can then be derived for the Laplace plane using Equations [18], [19], and [23]. Numerical inversion gives the dependencies in the t-plane. It therefore becomes possible to assess the effects of changes in k on the behavior of the system and the relaxation of the rate of reaction under potentiostatic conditions can be evaluated.

The application of Neumann's integral theorem also allows the evaluation of the potential distribution in the solution, as in the case of the discussion of the steady state[1,2]. However, in contrast to that case, the effects of this potential distribution on the chronoamperometric transient can only be evaluated in limiting cases. The potential distribution in the presence of excess support electrolyte is governed in the Laplace space by

$$\kappa \frac{\partial^2 \bar{\phi}}{\partial r^2} + \frac{\kappa}{r}\frac{\partial \bar{\phi}}{\partial r} + \kappa \frac{\partial^2 \bar{\phi}}{\partial z^2} = 0, \; \bar{\phi} = 0, \; r = \infty, \; z = \infty \qquad [28]$$

while the distribution of sources (for a cathodic reaction) over the disk is given by

$$\kappa \frac{\partial \bar{\phi}}{\partial z} = -zF\bar{Q}(\theta)$$

$$= \frac{-zF}{a\cos(\theta\ )} \left(\bar{d}_0(s) + \bar{d}_1(s)\cos(\theta) + \cdots + \bar{d}_n(s)\cos^n(\theta) \right) \qquad [29]$$

We therefore obtain the potential at the surface of the disk, $z = 0$, as

$$\bar{\phi}(r,s) = \frac{-zFa^2}{\kappa} \int_0^{\infty}\int_0^{\pi/2} \bar{Q}(\theta,s)\ J_0(\alpha r)\ J_0(\alpha a \sin(\theta)\ \sin(\theta)\ \cos\theta\ d\theta d\alpha$$

$$= \frac{-zFa}{\kappa} \int_0^{\infty} J_0(\alpha r)d\alpha \sum_{j=0}^{n} \int_0^{\pi/2} \bar{d}_j(s)\ J_0(\alpha a \sin(\theta)\ \sin(\theta)\ \cos^j\theta\ d\theta$$

$$= \frac{-zFa}{\kappa} \sum_{j=0}^{n} \bar{d}_j(s) e_j f_j\left(\frac{r}{a}\right) \qquad [30]$$

where e_j and $f_j\left(\frac{r}{a}\right)$ are given as in the steady state case[1] by

$$e_j = 2^{((j-1)/2)}\Gamma((j+1)/2) \qquad [31]$$

and

$$f_j\left(\frac{r}{a}\right) = \frac{\pi^{1/2}}{2^{((j+1)/2)}\Gamma((j+2)/2)a}\ {}_2F_1\left\{\frac{1}{2},-\frac{j}{2};\ 1;\ \frac{r^2}{a^2}\right\} \qquad [32]$$

Modification of [10] to take into account the distribution of potential in the solution gives

$$D\left(\frac{\partial C(r,t)}{\partial z}\right) = k\ \exp\left(\frac{\alpha\phi(r,t)F}{RT}\right)C^s$$

$$= k\ \exp\left(\frac{\alpha\phi(r,t)F}{RT}\right)(C^\infty - C(r,t)) \qquad [33]$$

where k is the value of the rate constant of the electrode reaction in the absence of any ohmic potential drops in the solution and C(r,t) is the inverse of the second term in quation [19]. A general Laplace transform of [33] can evidently only be obtained for sufficiently small perturbations of the potential and concentration for which

$$D\left(\frac{\partial C(r,t)}{\partial z}\right) \cong k\left(1 + \frac{\alpha\phi(r,t)F}{RT}\right)(C^{\infty} - C(r,t))$$

$$\cong k\left((C^{\infty} - C(r,t))\right) + \frac{k\alpha\phi(r,t)FC^{\infty}}{RT} \qquad [34]$$

giving

$$D\left(\frac{\partial \bar{C}}{\partial z}\right) = \frac{1}{a\cos(\theta)}\left(\bar{d}_0(s) + \bar{d}_1(s)\cos(\theta) + \cdots + \bar{d}_n(s)\cos^n(\theta)\right)$$

$$= \frac{kC^{\infty}}{s} - \frac{k}{Da}\sum_{j=0}^{n}\bar{d}_j\left(\frac{sa^2}{D}\right) e_j \int_0^{\infty} \frac{J_0(\alpha r)\, J_{\left(\frac{j+1}{2}\right)}(\alpha a)\, d(\alpha a)}{\left[\alpha^2 + \frac{s}{D}\right]^{1/2}(\alpha a)^{((j-1)/2)}}$$

$$- \frac{z\alpha F^2 kC^{\infty}a}{\kappa RT}\sum_{j=0}^{n} d_j(s) e_j f_j\left(\frac{r}{a}\right) \qquad [35]$$

Special solutions using [33] include those cases where the d_j can be approximated by linear functions in time

$$d_j = g_j + h_j(t) \qquad [36]$$

A further interesting case related to [36] is that of linear sweep voltammetry. We again restrict attention to the case of an irreversible reaction and, neglecting the effects of the tertiary current distribution, write [10] as

$$D\left(\frac{\partial \bar{C}(r,t)}{\partial z}\right) = k \exp\left(\frac{\alpha \nu t F}{RT}\right)(C^{\infty} - C(r,t))$$

$$= k \exp(\mu t)(C^{\infty} - C(r,t)) \qquad [37]$$

where k is the rate constant at t = 0. Laplace transformation of [37] gives

$$D\left(\frac{\partial \bar{C}}{\partial z}\right) = \frac{1}{a \cos(\theta)}\left(\bar{d}_0(s) + \bar{d}_1(s)\cos(\theta) + \cdots + \bar{d}_n(s)\cos^n(\theta)\right)$$

$$= \frac{kC^{\infty}}{(s-\mu)} - \frac{k}{Da}\sum_{j=0}^{n} \bar{d}_j(s-\mu)\, e_j \int_0^{\infty} \frac{J_0(\alpha r)\, J_{\left(\frac{j+1}{2}\right)}(\alpha a)\, d(\alpha a)}{\left[\alpha^2 + \frac{(s-\mu)}{D}\right]^{1/2} (\alpha a)^{((j-1)/2)}} \qquad [38]$$

an equation system which has to be solved in the t-domain where

$$\frac{1}{a\cos(\theta)}\left(d_0(t) + d_1(t)\cos(\theta) + \cdots + d_n(t)\cos^n(\theta)\right)$$

$$= kC^{\infty}\exp(\mu t) - \frac{kC^{\infty}\exp(\mu t)}{D^{1/2}\pi^{1/2}a}\sum_{j=0}^{n} e_j \int_0^t\!\!\int_0^{\infty} d_j(t-\tau)\,\frac{\exp(-D\alpha^2\tau)}{\tau^{1/2}}\,\frac{J_0(\alpha r)J_{\left(\frac{j+1}{2}\right)}(\alpha a)\,d(\alpha a)\,d\tau}{(\alpha a)^{((j-1)/2)}}$$

$$= kC^{\infty}\exp(\mu t) - \frac{kC^{\infty}\exp(\mu t)}{D^{1/2}\pi^{1/2}a}\sum_{j=0}^{n} e_j \int_0^t\!\!\int_0^{\infty} d_j(\tau)\,\frac{\exp(-D\alpha^2(t-\tau))}{(t-\tau)^{1/2}}\,\frac{J_0(\alpha r)J_{\left(\frac{j+1}{2}\right)}(\alpha a)\,d(\alpha a)\,d\tau}{(\alpha a)^{((j-1)/2)}}$$

[39]

<u>c.e and e.c. catalytic reactions in the steady state</u>

We first consider the behavior of the c.e. reaction

$$A \underset{k_2'}{\overset{k_1'}{\rightleftarrows}} B \qquad [i]$$

$$B \xrightarrow{ze^-} C \qquad [ii]$$

in the steady state with the reactant A present in excess concentration. Then if C denotes the concentration of B, the diffusion of this species is governed

by

$$D\frac{\partial^2 C}{\partial r^2} + \frac{D}{r}\frac{\partial C}{\partial r} + D\frac{\partial^2 C}{\partial z^2} + k_1' C_A - k_2 C$$

$$\cong D\frac{\partial^2 C}{\partial r^2} + \frac{D}{r}\frac{\partial C}{\partial r} + D\frac{\partial^2 C}{\partial z^2} + k_1 - k_2 C = 0 \qquad [40]$$

Equation [40] is subject to the boundary condition

$$C = C^\infty = k_1/k_2,\ r = \infty,\ z = \infty,\ \text{all } t. \qquad [41]$$

and we again consider initially the simplest condition at the electrode surface

$$C = 0,\ 0 < r < a,\ z = 0,\ \text{all } t \qquad [42]$$

and with

$$D\frac{\partial C}{\partial z} = 0,\ r > a,\ z = 0,\ \text{all } t \qquad [43]$$

The similarity of Equation [40] in standard form

$$\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial z^2} - \frac{k_2 C}{D} + \frac{k_1}{D} = 0 \qquad [44]$$

is apparent and we obtain the solution for the concentration of B as

$$C(r,z,k_2) = \frac{k_1}{k_2} + \frac{1}{D}\int_0^\infty \frac{\exp\left(-\left[\alpha^2 + \frac{k_2}{D}\right]^{1/2} z\right)}{\left[\alpha^2 + \frac{k_2}{D}\right]^{1/2}} J_0(\alpha r)\alpha d\alpha \int_0^\infty Q(\rho,k_2)J_0(\alpha\rho)\rho d\rho \qquad [45]$$

By analogy to the distribution of sinks for the chronoamperometric transient we assume that for the c.e. reaction we can write

$$-Q(\theta) = \frac{-1}{a\cos(\theta)}\left(d_0(k_2) + d_1(k_2)\cos(\theta) + \cdots + d_n(k_2)\cos^n(\theta)\right) \qquad [46]$$

where the d_j are now functions of k_2. Then at $z = 0$ we obtain

$$C(r,k_2) = \frac{k_1}{k_2} - \frac{1}{Da}\sum_{j=0}^{n} d_j(k_2)\, e_j \int_0^{\infty} \frac{J_0(\alpha r) J_{\left(\frac{j+1}{2}\right)}(\alpha a)\, d(\alpha a)}{\left[\alpha^2 + \frac{k_2}{D}\right]^{1/2} (\alpha a)^{((j-1)/2)}} \qquad [47]$$

Then, if the boundary condition [42] applies, the (n+1) coefficients $d_j(k_2)$ can be derived by solving the set of equations

$$\frac{1}{Da}\sum_{j=0}^{n} d_j(k_2)\, e_j \int_0^{\infty} \frac{J_0(\alpha r_k) J_{\left(\frac{j+1}{2}\right)}(\alpha a)\, d(\alpha a)}{\left[\alpha^2 + \frac{k_2}{D}\right]^{1/2} (\alpha a)^{((j-1)/2)}} = \frac{k_1}{k_2} \qquad [48]$$

at (n+1) radial positions. A working curve of the kinetically limited flux can then be constructed from

$$R(k_2) = 2\pi a \sum_{j=0}^{n} \frac{d_j(k_2)}{(j+1)} \qquad [49]$$

Mass transfer of the reactant species F in the e.c. (catalytic) reaction scheme

$$E + ze \rightleftarrows F \qquad \text{(iii)}$$

$$F + G \xrightarrow{k_2} E + H \qquad \text{(iv)}$$

is described by

$$D \frac{\partial^2 C}{\partial r^2} + \frac{D}{r}\frac{\partial C}{\partial r} + D \frac{\partial^2 C}{\partial z^2} - k_2' C_G C$$

$$\cong D \frac{\partial^2 C}{\partial r^2} + \frac{D}{r}\frac{\partial C}{\partial r} + D \frac{\partial^2 C}{\partial z^2} - k_2 C = 0 \qquad [50]$$

in the presence of excess of the substrate G. Provided the reaction (iii) can be driven sufficiently hard in the forward direction, [50] will be subject to the boundary conditions

$$C = C^{\infty},\ 0 < r < a,\ z = 0,\ \text{all } t \qquad [51]$$

$$C = 0,\ r = \infty,\ z = \infty,\ \text{all } t \qquad [52]$$

where C^{∞} is the concentration of species E in the bulk of the solution. With a distribution of sources over the disk having the form [46], we therefore

obtain the concentration

$$C(r,z,k_2) = \frac{1}{D}\int_0^\infty \frac{\exp\left(-\left[\alpha^2+\frac{k_2}{D}\right]^{1/2} z\right)}{\left[\alpha^2+\frac{k_2}{D}\right]^{1/2}} J_0(\alpha r)\alpha d\alpha \int_0^\infty Q(\rho,k_2)J_0(\alpha\rho)\rho d\rho \qquad [53]$$

and at z = 0

$$C^\infty = \frac{1}{Da}\sum_{j=0}^{n} d_j(k_2)\ e_j \int_0^\infty \frac{J_0(\alpha r)J_{\left(\frac{j+1}{2}\right)}(\alpha a)\ d(\alpha a)}{\left[\alpha^2+\frac{k_2}{D}\right]^{1/2}(\alpha a)^{((j-1)/2)}} \qquad [54]$$

The $d_j(k_2)$ are evaluated by solving this set of equations and the working curve of the kinetically limited flux can again be constructed using [49].

The use of the boundary conditions [42] and [51] is, however, unrealistic for the same reasons that [14] is unrealistic for the evaluation of the chronoamperometric transients. In reality, the electron transfer reactions (ii) and (iii) will take place at finite rates and the e.c. (catalytic) reactions especially will be subject to the effects of the distribution of potential in the solution. It is better therefore to seek to predict the complete form of the polarization plots taking into account all these effects. It is, in fact, possible to achieve such a complete description of the systems

since we are considering their behavior in the steady state; we restrict attention here to the case where the electron transfer processes are irreversible so that they can be described by the boundary condition [10].

The distribution of potential in the solution follows as outlined above and we obtain at z = 0

$$\phi(r,k_2) = \frac{-zFa}{\kappa} \sum_{j=0}^{n} d_j(k_2)e_j f_j\left(\frac{r}{a}\right) \qquad [55]$$

Application of the boundary conditions [10] to the reaction step (ii) in the c.e. mechanism taking into account [55] gives

$$D\left(\frac{\partial C(r,k_2)}{\partial z}\right) = \frac{1}{a\cos(\theta)}\left(d_0(k_2) + d_1(k_2)\cos(\theta) + \cdots + d_n(k_2)\cos^n(\theta)\right)$$

$$= k\exp\left(\frac{\alpha\phi(r,k_2)F}{RT}\right) C^s$$

$$- k \exp\left[\frac{-z\alpha F^2 a}{\kappa RT}\sum_{j=0}^{n} d_j(k_2) e_j f_j\left(\frac{r}{a}\right)\right] \cdot \left\{ \frac{k_1}{k_2} \right. -$$

$$\left. - \frac{1}{Da}\sum_{j=0}^{n} d_j(k_2)\ e_j \int_0^\infty \frac{J_0(\alpha r) J_{\left(\frac{j+1}{2}\right)}(\alpha a)\ d(\alpha a)}{\left[\alpha^2 + \frac{k_2}{D}\right]^{1/2} (\alpha a)^{((j-1)/2)}} \right\} \qquad [56]$$

where k is the rate constant for reaction (iii) for zero ohmic potential at the surface of the disk. The non-linear equation system [56] can be solved at (n+1) radial positions for the (n+1) required coefficients d_j in the same way as has been described for the case of the tertiary current distribution in simple redox reactions at disk electrodes[1,2].

In a similar way the application of [10] and [55] to the reaction step (iii) of the e.c. (catalytic) mechanism gives the equation system

$$\frac{1}{a\cos(\theta)}\left(d_0(k_2) + d_1(k_2)\cos(\theta) + \cdots + d_n(k_2)\cos^n(\theta)\right)$$

$$- k \exp\left[\frac{-z\alpha F^2 a}{\kappa RT}\sum_{j=0}^{n} d_j(k_2) e_j f_j\left(\frac{r}{a}\right)\right] \cdot \left\{ C^\infty \right. -$$

$$- \frac{1}{Da}\sum_{j=0}^{n} d_j(k_2)\, e_j \int_0^{\infty} \frac{J_0(\alpha r) J_{\left(\frac{j+1}{2}\right)}(\alpha a)\, d(\alpha a)}{\left[\alpha^2 + \frac{k_2}{D}\right]^{1/2} (\alpha a)^{((j-1)/2)}} \Bigg\} \qquad [57]$$

where k is now the rate constant for reaction (iii) (assumed here to be irreversible) for zero ohmic overpotential in the solution. The coefficients d_j derived from [56] and [57] are naturally also functions of k (i.e. of the standard rate constant, of α and of the overpotential) as well as of the solution conductivity κ. The polarization curves can therefore be completely described for this model (and indeed other models) using

$$R(k_2,k,\kappa) = 2\pi a \sum_{j=0}^{n} \frac{d_j(k_2,k,\kappa)}{(j+1)} \qquad [58]$$

Discussion

It can be seen that the application of Neumann's integral of two parameters (the radial and s-dependence of the surface source/sink over the disk electrode) allows a more comprehensive discussion of the chronoamperometric transients than has been achieved to date using other analytical as well as simulation techniques(4,7,9-16). In particular, since Neumann's integral leads to a relation between the assumed form of the flux and the concentration oat the surface (Equations [17] and [18]) it becomes possible to derive the transient for boundary conditions such as [10] which are more realistic than the assumption of zero or constant surface concentration, [14], which has been used to date.; for example, Equation [2 leads to the definition of the potentiostatic relaxation behavior of disk

electrodes.

We have pointed out elsewhere[4,8,16] that the combined effects of the finite rates of electrode reactions and of the potential distribution in the solution must make the distribution of the flux over the surface much more uniform than that predicted using the boundary condition [14]. Indeed, the predictions of a model of uniform surface flux and zero average surface concentration[4,16] has been shown to be in close accord with experimental measurements[7]. While the methodology outlined here allows a systematic exploration of one of the effects, that of the finite rates of electrode reactions, Equation [10], the exploration of the effects of changes in the potential in the solution unfortunately remains restricted to the discussion of the relaxation behavior[17] (cf. Equations [34] and [35]); in effect, we reach the limits of analytical techniques. However, it does become possible to develop a complete discussion of linear sweep voltammetry and of cyclic voltammetry[17], as has been outlined for the first case above, provided the effects of the tertiary current distribution are neglected.

It has been shown previously that there are no restrictions in the discussion of the steady state behavior of simple electrode processes[1,2]. The discussion presented here shows that this is equally true for electrode processes coupled to reactions in solution such as for the c.e. and e.c (catalytic) mechanisms; a complete description of such systems can be developed. Comparisons of the predictions with those based on other models and methods of analysis[4,18,19,20] as well as extensions to other reaction schemes will be presented elsewhere[21].

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Glossary of Symbols

a	Disk radius, cm
b_i	Weighting function series coefficients
c_i	Fourier coefficients, mols $(cm\ s)^{-1}$
d_i	Fourier coefficients, mols $(cm\ s)^{-1}$
e_i	Fourier constant terms
f_i	Fourier series integral terms, cm^{-1}
C	Concentration, mols cm^{-3}
C^{∞}	Bulk concentration, mols cm^{-3}
C_{Av}	Average concentration, mols cm^{-3}
C^{s}	Surface concentration, mols cm^{-3}
D	Diffusion coefficient, $cm^2 s^{-1}$
F	Faraday constant, 96485 C equivalent^{-1}
i_0	Exchange current density, A cm^{-2}
i	Current, A
I	Current density, A cm^{-2}
J_i	Bessel functions
k	Heterogeneous rate constant, cm s^{-1}
k	Homogeneous rate constant, various
k_0	Heterogeneous standard rate constant, cm s^{-1}
k_1, k_2	Homogeneous rate constants, various types
Q	Flux, mols $cm^{-2}s^{-1}$
R	Gas constant, 8.314 J $mols^{-1}K^{-1}$
r	Radial coordinate, cm
s	Laplace transform variable
T	Temperature, K

z	Coordinate normal to plane of disk, cm
z	Charge of an ion
α	Transfer coefficient (when in exponent)
α	Continuous dummy integration variable.
ϕ	Solution potential, V
ρ	a sin(θ), cm
κ	Solution Conductivity, $ohms^{-1}cm^{-1}$
η	Overpotential, V
τ	Laplace transform dummy integration variable

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